ZIRCONIUM AND HAFNIUM EXTRACTION USING CROWN ETHERS - A MODEL SYSTEM FOR THE STUDY OF RUTHERFORDIUM

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Introduction

Recently, the fast, automated liquid-liquid extraction system SISAK was successfully used to study the chemical behavior of element 104, rutherfordium [1]. This was made possible by coupling the SISAK system to the Berkeley Gas-filled Separator (BGS). The BGS was used to achieve a physical pre-separation of the desired species from the beam and unwanted reaction products. This pre-separation reduced the background due to the scattered beam and other reaction products substantially, and allowed for an easier detection of rutherfordium atoms. The lack of interfering reaction products offers several advantages for the design of chemistry experiments with transactinides. In addition to simplifying the detection and data analysis, it allows the use of different classes of extraction systems in future experiments with SISAK or other automated systems, as well as manual extraction experiments.

In the past, it was necessary to select extraction systems that removed all interfering reaction products and left only the element of interest. Consequently, a very high decontamination factor between the element of interest and interfering nuclides had to be favored over a high selectivity between the different homologs within the group being studied. When using a physical pre-separator, selectivity between the members of the same group of the periodic table can now be favored over efficient separation from elements belonging to other groups when designing extraction systems for future experiments [2]. As a result the usefulness of previously used extraction systems should be reevaluated and other classes of extraction systems can now be considered as well.

Based on the first successful experiments with pre-separated rutherfordium isotopes, it was decided to start searching for different highly selective extraction systems that could be used to study the chemistry of rutherfordium. Some of the extraction systems under investigation use macrocyclic ligands, such as crown ethers. The high selectivity of these systems is used in a multitude of applications in analytical and technical chemistry. The coordination chemistry of macrocyclic ligands and alkali and earth alkali metals has been studied in depth [3], and these ligands are commonly applied for the separation of various metal ions [4].

The kinetic of the reaction is in important factor in developing suitable extraction systems for chemistry experiments with transactinide elements. The reaction should reach equilibrium as fast as possible. The size of the organic molecules used as ligands can have a large effect on the

kinetics of the reaction. The use of different crown ethers, e.g., dibenzo-18-crown-6 and dicyclohexano-18-crown-6, for the separation of zirconium and hafnium has been reported previously in the literature [5, 6], but none of these studies were conducted on a time scale short enough to ensure that the reaction kinetics is fast enough to allow the study of rutherfordium.

Experimental

In this work, the extraction of zirconium and hafnium with dibenzo-18-crown-6 (DB18C6) and dicyclohexano-18-crown-6 (DC18C6) from various concentrations of hydrochloric acid was studied using isotopes with short and medium half-lives. The distribution ratios for the elements were determined as a function of acid and ligand concentration. The kinetics of the reaction was studied by varying the contact time during mixing and the time allowed for phase separation.

The online experiments were performed at the 88-inch cyclotron at LBNL using the short-lived isotopes ^{85}Zr ($T_{1/2}$ = 7.9 m) and ^{169}Hf ($T_{1/2}$ = 3.25 m). The isotopes were produced by bombarding a ^{nat}Gd with an ^{18}O^{4+} beam and a ^{124}Sn target with a ^{50}Ti^{11+} beam, respectively. The two beams were delivered by the cyclotron as a cocktail beam. The use of this ion cocktail allowed for the fast switching between the two beams. It ensured together with the use of an adjustable target ladder in the BGS that experiments with zirconium and hafnium could be performed almost simultaneously and under virtually the same experimental conditions.

The zirconium and hafnium isotopes produced were separated from the beam and interfering reaction products using the BGS. After traveling through the BGS, the products passed through a thin Mylar window into the Recoil Transfer Chamber (RTC) [7]. Inside the RTC, the recoils were thermalized in helium and transported to the chemistry setup using a potassium chloride aerosol gas-jet. The gas-jet was operated with an average flow rate of 1.8 L/min and a pressure of 1.2 bar.

The aerosols containing the radionuclides were transported over a distance of ~15 meters and deposited on platinum foils. The aerosol residue was dissolved in 50 μL HCl of appropriate concentration and transferred to a centrifuge cone containing additional 3950 μL of the same acid. The aqueous phase was mixed with an equal volume of crown ether diluted in dichloromethane. Phases were vigorously mixed for 20 seconds and centrifuged for 20 seconds. Afterwards a 3-mL aliquot was taken from each phase and assayed using a HPGe γ-ray detector. Offline experiments were performed using ^{88}Zr ($T_{1/2}$ = 83.4 d) and ^{175}Hf ($T_{1/2}$ = 70.0 d) as radiotracers to study the effect of longer mixing times on the distribution ratio.

Results

Figure 1 shows the yield for the extraction of Zr and Hf with 0.900 M DB18C6 from 8.0 – 10.5 M HCl. Both elements are extracted, the extraction yield increases with increasing acid concentration. Zr extraction starts at HCl concentrations above 8.0 M and reaches a maximum of 89%. Hf extraction begins between 8.5 and 9.0 M and reaches a maximum value of 84%. The separation factor, defined as the ratio of extraction yields for the two elements, has its maximum at the lowest acid concentration studied and decreases with increasing acid concentration.

The yield for the extraction of Zr and Hf with 0.025 M DC18C6 from 7.0 – 10.5 M HCl can be seen in figure 2. Zr and Hf are both extracted with the extraction yield increasing sharply between 7.0 and 8.5 M. It generally reaches higher values than with DB18C6. As with DB18C6

the Hf extraction starts at higher acid concentration compared to Zr. The extraction yield reaches a maximum of 91% for Zr and 88% for Hf.

Both crown ethers investigated show great potential as extractants for the study of the chemical behavior of rutherfordium. They show a stronger tendency to form complexes with Zr than with Hf. Suitable experimental conditions can be chosen to separate Zr from Hf. Using similar conditions when studying the chemistry of rutherfordium, should answer the question whether Rf behaves more like Zr or Hf in this chemical system.

Additional data on the extraction behavior of Zr and Hf, the influence of the ligand concentration, and the results of the study of the reaction kinetics will be presented at the conference.
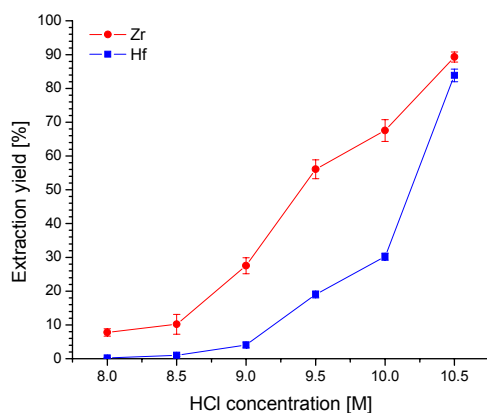

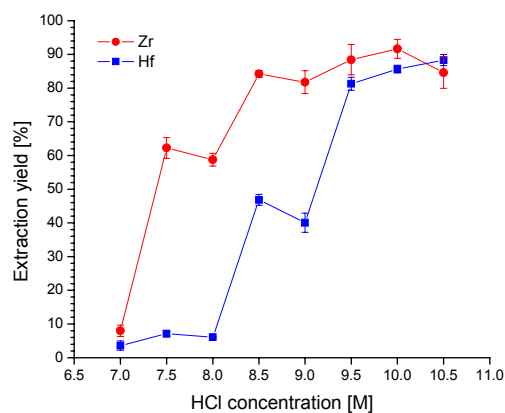Figure 1. Zr and Hf extraction from 8.0 – 10.5 M HCl into 0.900 M DB18C6 in CHCl$_2$.

Figure 2. Zr and Hf extraction from 7.0 – 10.5 M HCl into 0.025 M DC18C6 in CHCl$_2$.

Acknowledgement:

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